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Benchmark thermodynamic properties of alkanediamines: Experimental and theoretical study

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ABSTRACT

Vapor pressures of (*dl*)-1,2-propanediamine and 2-methyl-1,2-propanediamine were measured using the transpiration method. Molar enthalpies of vaporization were derived from the vapor pressure temperature dependence. Thermodynamic data on alkanediamines available in the literature were collected and treated uniformly. Consistency of the experimental data set for alkanediamines was evaluated with group-contribution and quantum-chemical methods.

The standard molar entropy of formation and the standard molar Gibbs function of formation have been calculated. Vaporization and formation enthalpies of alkanediamines of benchmark quality are recommended for practical thermochemical calculations and validation of empirical and theoretical methods.

1. Introduction

Quantum chemical methods have become indispensable research tools in chemistry and materials science. They offer the real promise of being able to complement experiment as a means to uncovering and exploring new chemistry [1]. Experimentalists rely increasingly on these methods to interpret and validate their findings. Demonstration of agreement between the independent experimental and computed results can provide strong validation for both results and to establish thermochemical data of benchmark quality. In the context of our experimental and computational studies of N-containing compounds [2–6] we have found that standard molar enthalpies of formation $\Delta_f H^\circ_m$ (g, T = 298.15 K) for 1,2-propanediamine, 1,2-butanediamine, and 2-methyl-1,2-propanediamine (see figure 1) calculated by using high-level G3MP2 calculations were systematically less negative in comparison to experimental values [7,8]. At a first glance, the experimental data in reference [8] were of seemingly impeccable quality. However, a more detailed analysis of primary vapor pressures reported in reference [8] have revealed some shortcomings in data treatment, leading to systematically erroneous vaporization enthalpies and, as a consequence, erroneous $\Delta_f H^\circ_m$ (g, T = 298.15 K) values as reported in the modern databases. In order to ascertain the available experimental data we have performed additional vapor pressure studies of (*dl*)-1,2-propanediamine and methyl-1,2-propanediamine by using the transpiration method. The aim of this work was the experimental and computational study of the alkanediamines presented in figure 1 in order to evaluate available thermochemical properties and to recommend a dataset of benchmark quality, capable for validation of quantum-chemical methods.

2. Materials and methods

2.1. Materials

Samples of (*dl*)-1,2-propanediamine and 2-methyl-1,2-propanediamine were of commercial origin. They were further purified by fractional distillation with a spinning-band column in vacuum. No impurities (greater than 0.001 mass fraction) could be detected in the samples used for the vapor pressure measurements. The degree of purity was determined using a GC on a HP-5 capillary column, column length of 30 m, inside diameter of 0.32 mm, and film thickness of 0.25 μm. Provenance and purity of compounds prepared for vapor pressure measurements are given in table S1.

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